

PATENT SPECIFICATION

(11)

1 304 072

NO DRAWINGS



1 304 072

- (21) Application No. 20657/70 (22) Filed 29 April 1970
 (23) Complete Specification filed 19 April 1971
 (44) Complete Specification published 24 Jan. 1973
 (51) International Classification C23C 13/02
 (52) Index at acceptance
 C7F 1V1 2A 2H 2L 2U 2Y 2Z3 3E 4N 6E1B 6F1
 (72) Inventors DAVID MANN
 ROBERT CLIVE LANSBURY

(54) IMPROVEMENTS IN OR RELATING TO METALLISED FILMS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London, S.W.1., a British Company do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to the production of metallised films, to improved metallised films, and in particular to metallised films of crystalline polyesters and polyolefines.

According to the present invention we provide a process for the production of a metallised organic thermoplastic polymeric film by coating at least one surface of a film with a resin which contains an isocyanate-ended polyurethane of average molecular weight greater than 1000 and an organic polyisocyanate containing isocyanurate rings and having an average of more than two isocyanate groups per molecule, drying the coating on the film, and depositing a layer of metal on the coated surface of the film.

The isocyanate-ended polyurethane used in the process of the present invention should be cured on the film so that it will become adhesively bonded to both the film and the metal layer. These polyurethanes may be cured by heating after they have been applied to the film, and this may be effected before, during or after the deposition of the layer of metal.

For certain films, particularly polyolefine films, we prefer that the surface of the film is subjected to a treatment to improve its bonding properties before the coating of the isocyanate-ended polyurethane is applied. This treatment may be a physical or a chemical treatment which oxidises the film surface and thus improves its bonding properties. Examples of suitable chemical treatments are to treat the surface of the film with oxidising agents such as chromic acid in sulphuric acid, or hot nitric acid, or to

expose the surface to ozone. Alternatively, the surface of the film may be subjected to exposure to corona discharge (such treatment is described in British Patent Specification No. 715,914), to ionising radiation, or to a flame for a sufficient time to cause superficial oxidation but not long enough to cause distortion of its surface. The preferred treatment, because of its effectiveness and simplicity, is a high voltage electric stress accompanied by corona discharge. The treated surface of the film is then overcoated with the resin. The preparation of the resins which are coated onto the surface treated film in the process of the present invention is described in our British Patent No. 1,052,042.

The isocyanate-ended polyurethanes of molecular weight more than 1000 may be obtained by interaction of a molecular excess of an organic polyisocyanate with a polyhydroxy compound of molecular weight greater than 400, and preferably between 400 and 5,000, optionally in conjunction with a hydroxy compound of molecular weight below 400.

Examples of polyhydroxy compounds of molecular weight greater than 400, are polyethers, polyetherthioethers, polyesters and polyacetals. These polymers should preferably be linear or only slightly branched. Examples of suitable polyethers are polymers and copolymers of cyclic oxides, for example 1:2-alkylene oxides such as ethylene oxide, epichlorohydrin, 1:2-propylene oxide, 1:2-butylene oxide and 2:3-butylene oxide, oxycyclobutane and substituted oxycyclobutanes, and tetrahydrofuran. Alternatively, polyethers such as are prepared, for example, by the polymerisation of an alkylene oxide in the presence of a basic catalyst and water, glycol, a polyhydric alcohol such as a glycerol, or a primary monoamine or mixtures of such polyethers may be used. The preferred polyethers are

[Price 25p]

polypropylene ether polymers which have an equivalent weight per hydroxyl group of between 200 and 1500.

If a polyester is used it may be made by conventional means from for example dicarboxylic acids and dihydric alcohols. Suitable dicarboxylic acids are succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, phthalic, isophthalic, and terephthalic acids and mixtures of these. Small proportions of polycarboxylic acids such as trimelic acid may also be used. Suitable glycols are ethylene glycol, 1:2-propylene glycol, diethylene glycol, dipropylene glycol, trimethylene glycol, 1:2-, 1:3-, 2:3- and 1:4-butylene glycols, neopentyl glycol, pentaerythritol glycol, and hexamethylene glycol and mixtures of these. The preferred polyesters have melting points below 60°C and are derived from glycols having two to eight carbon atoms and dicarboxylic acids having from four to ten carbon atoms. Particularly suitable are polyesters of molecular weight between 500 and 2500 derived from such dicarboxylic acids, especially adipic acid, and a glycol or mixture of glycols at least one of which contains at least one secondary hydroxyl group.

The hydroxy compound of molecular weight below 400 which may optionally be condensed with the polyisocyanate in conjunction with the polyhydroxy compound may be a mono-functional alcohol such as methanol, ethanol or butanol, or a glycol such as ethylene glycol, diethylene glycol, butylene-1:3-glycol, trimethylene glycol, tetramethylene glycol, propylene glycol, dipropylene glycol, neopentyl glycol and thiodiglycol, or a polyol such as glycerol, trimethylolpropane, hexamethylenetriol, pentaerythritol, sorbitol or mannitol.

The organic polyisocyanate which is interacted with the hydroxy compound of molecular weight greater than 400 to prepare the isocyanate-ended polyurethane may be for example an aliphatic or cycloaliphatic diisocyanate. Alternatively, it may be a polyurethane polyisocyanate obtained by interaction of excess of a polyisocyanate, such as those hereinbefore described, with a polyhydroxy compound such as ethylene glycol, butylene glycol, diethylene glycol, neopentyl glycol, trimethylolpropane, glycerol or hexanetriol. If desired the polyisocyanate may be polymerised to afford polyisocyanates containing isocyanurate rings.

The preparation of the isocyanate-ended polyurethane is carried out in conventional manner usually by heating the ingredients together at a temperature between 40°C and 160°C and preferably between 70°C and 130°C. The reaction may be carried out in a solvent inert to isocyanates, particularly suitable solvents being esters, ketones and halogenated hydrocarbons. It is usually pre-

ferred that the reaction is carried out under slightly acidic conditions to minimise side reactions leading to high viscosity products. Although polyisocyanates are usually acidic, it may be necessary, in order to ensure acidity of the reaction mixture, to add an acidic compound such as a mineral or organic acid or acid halide in amount equivalent to 0.005% calculated as halide on the weight of polyisocyanate present. In order to ensure that the polyurethane possesses terminal isocyanate groups the amount of polyisocyanate used in its preparation should be such that there is an excess of isocyanate groups over that required to react with the hydroxyl groups present.

Particularly useful isocyanate-ended polyurethanes are obtained from organic polyisocyanates and polyesters or mixtures of polyesters with a hydroxy compound of low molecular weight wherein the polyester or mixture possesses an average of not more than three hydroxyl groups per molecule, and the organic polyisocyanate is a diisocyanate used in such amount that there are from 1.05 to 2.0 and preferably from 1.2 to 1.5 isocyanate group for each hydroxyl group.

The organic polyisocyanates containing isocyanurate rings used in our invention may be prepared by the polymerisation of polyisocyanates in the presence of the catalysts known to assist this polymerisation. For example a diisocyanate either alone or in a suitable inert solvent may be heated with a basic catalyst such as an aliphatic tertiary amine, a basic metallic compound such as an alkali or alkaline earth metal oxide, hydroxide, carbonate, alcoholate or phenate, an alkali metal derivative of an enolisable compound or a metallic salt of a weak organic acid. Co-catalysts may be used, such as alcohols, phenols, mono-N-substituted carbamic esters or cyclic oxides.

The organic polyisocyanate containing isocyanurate rings may be derived from an aliphatic or cycloaliphatic diisocyanate such as may be used in preparing the isocyanate-ended polyurethane.

The resins which are coated onto the film in the process of our invention may be obtained by blending the ingredients together in any order. The relative proportions of isocyanate-ended polyurethane and isocyanurate polyisocyanates are preferably within the range from 12:1 to 1:12 by weight, but proportions outside this range may be used if desired.

Our preferred resins are those prepared by reaction of polyethylene propylene adipate with tolylene diisocyanate in a suitable solvent, and then reacting the product of this reaction with an equal amount by

weight of an organic polyisocyanate containing isocyanurate rings dissolved in a suitable solvent.

The coating resin used in the process of this invention may be modified by blending with other suitable materials. For example, the water resistance of the coated film may be improved if the resin is blended with another thermosetting resin e.g. melamine formaldehyde or a urea formaldehyde or epoxy condensation resin. The processability may be improved if the resin is blended with a small amount of a polyol. Alternatively the coating resin may be blended with an acrylic resin such as those described in our British Patent No. 1,134,876.

The resin may be applied to one or both surfaces of the film and may be applied as a dispersion or as a solution. The dispersant or solvent in which the resin is applied to the film should be chosen so that it does not react with isocyanates. Examples of suitable organic solvents include aromatic hydrocarbon solvents such as xylene, urethane grades of esters and ketones such as ethyl acetate, ethoxyethyl acetate, butoxyethyl acetate, methylethylketone, methylisobutylketone, or methoxyhexanone, or mixtures of such solvents as is appropriate.

After the coating of the resin has been applied to the treated surface or surfaces of the film it should be dried off on the film before the metal layer is deposited. The resin is at least partially cured during the drying operation so that it adheres to the base film and will not be removed by the application of the metal layer. The process of this invention is particularly applicable to applying metal coatings to oriented films and as oriented films tend to be dimensionally unstable at elevated temperatures it is desirable that the time to which the film is subjected to elevated temperatures during the process of the present invention be as short as possible. Similarly it is desirable that the temperatures to which the film is subjected should be as low as possible consistent with satisfactory adhesion of the metal layer to the film. We prefer that the resin be dried off on the film at a temperature in the range 60°C to 120°C, preferably 60°C to 90°C.

When the coating of the resin has been dried off on the film the metal layer may then be deposited on the film.

Methods are well known for the application of metal layers to films and any of these methods may be used. Our preferred method consists of directing a stream of metal vapour on to the surface of the film by vacuum evaporation techniques. In these techniques the metal is heated in a high vacuum typically in the range 10^{-3} to 10^{-5} torr, to a temperature which exceeds its melting point such that the vapour pressure

of the metal is greater than approximately 10^{-3} torr. Under these conditions the metal vaporises emitting molecular rays in all directions. These molecular rays impinge upon the substrate, condense and so form a thin metallic film over the substrate.

The process of the present invention is applicable to the deposition of all metal coatings on to thermoplastic films and is particularly applicable to the deposition of zinc, aluminium, copper, chromium, nickel, silver and gold.

The present invention is also concerned with metallised films produced by the process of the present invention and therefore provides an organic thermoplastic film coated with a metal layer said metallised film being provided with an intermediate resin coating between the film and the metal layer which comprises an isocyanate-ended polyurethane of average molecular weight greater than 1000 and an organic polyisocyanate containing isocyanurate rings and having an average of more than two isocyanate groups per molecule.

The process and product of the present invention relate to films of any organic thermoplastic polymeric material, for example polymers and copolymers of alpha olefines such as ethylene, propylene, butene and 4-methyl pentene-1, linear polyesters such as polyethylene terephthalate and polyethylene-1,2-diphenoxymethane-4,4'-dicarboxylate, and polymers and copolymers containing vinyl chloride. The films which are metallised by this invention may be unoriented or may be oriented in one or both of two mutually perpendicular directions in the plane of the film and if oriented in both directions the orientation may be equal in those directions or unequal, for example with the higher degree of orientation in a preferred direction (usually the longitudinal direction). The oriented films may be heat set either before or after the coating treatment, and the resin coating may be applied before or after the film is stretched to orient it.

Although we prefer that the resin coating be applied to an uncoated film substrate, the substrate may be, if desired, a composite substrate, such as a polypropylene film to which has been applied a coating layer of polyvinylidene chloride.

Our invention is particularly applicable to oriented films of polypropylene and polyethylene terephthalate and the metallised films are useful for the manufacture of capacitors or may be slit to produce decorative textile yarns. Textile yarns, may be produced by slitting a film along its length and it is important that these yarns have high strength along the axis of the yarn and thus films with a higher degree of orientation along their length are preferred

for the production of yarns.

The invention is illustrated by reference to the following Examples.

EXAMPLE 1

By means of a roller coating apparatus a biaxially oriented polypropylene film containing conventional antistatic and anti-blocking additives totalling about 1.4% by weight was coated with a 5% by weight solution in methylethylketone of a mixture of an isocyanate-ended, polyester-based urethane prepolymer and a polyisocyanate containing isocyanurate rings—commercially available as 'Daltosec' 1450 ('Daltosec' is a Registered Trade Mark of Imperial Chemical Industries Limited). The average weight of coating deposited on the film surface was about 0.25 g/m².

The coated film surface was cured by drying in a circulating-air oven at 90°C for about 30 seconds, and a layer of aluminium was then deposited on the cured surface by a conventional vacuum metallising technique.

To test the adhesion of the aluminium layer to the coated substrate, a 25 mm wide strip of "Sellotape" 1109 adhesive tape ("Sellotape" is a Trade Mark) was pressed into contact with the aluminium coated surface, and then pulled sharply away from the substrate. By visual inspection of the adhesive tape it was apparent that virtually none of the aluminium coating layer had been removed from the substrate.

By comparison, when an identical polypropylene film was directly metallised with aluminium, without the application of an intermediate resin coating, about 90% of the aluminium was removed by the adhesive tape test.

EXAMPLE 2

The procedure of Example 1 was repeated, using as substrate a biaxially oriented polypropylene film containing no antistatic or other additives.

When submitted to the adhesive tape test described in Example 1, approximately 50% of the aluminium coating was removed, whereas in a comparative test in which the aluminium was deposited directly onto a polypropylene substrate, approximately 90% of the aluminium layer was removed by the adhesive tape.

EXAMPLE 3

The procedure of Example 2 was repeated, but in this Example the substrate was metallised with silver by a conventional vacuum deposition technique.

When tested by the adhesive tape method outlined in Example 1, approximately 50% of the silver layer was removed, whereas about 95% of the silver layer was removed from a similar substrate which had not been primed with an intermediate resin coating.

EXAMPLE 4

A biaxially oriented polypropylene film, free from additives, was coated with a methylethylketone solution containing 5% by weight of 'Daltosec' 1450 ('Daltosec' is a Registered Trade Mark) and 0.1% by weight of a beta diethylamino ethanol catalyst—available as 'Daltogen' 50 ('Daltogen' is a Registered Trade Mark of Imperial Chemical Industries Limited). The average weight of the coating deposited on the film surface was about 0.25 g/m².

After curing in an air oven at 60°C for 30 seconds, a layer of aluminium was deposited on the coated substrate by a conventional vacuum metallising technique.

When tested by the adhesive tape test outlined in Example 1, approximately 50% of the aluminium layer was removed, whereas in a comparative test using an unprimed substrate approximately 90% of the aluminium layer was removed.

EXAMPLE 5

The procedure of Example 4 was repeated using silver in place of aluminium.

When tested by the technique outlined in Example 1 approximately 50% of the silver was removed from the substrate, whereas in a comparative test on an unprimed substrate approximately 95% of the silver layer was removed.

WHAT WE CLAIM IS:

1. A metallised film comprising an organic thermoplastic film coated with a metal layer, said metallised film being provided with an intermediate resin coating between the film and the metal layer which comprises an isocyanate-ended polyurethane of average molecular weight greater than 1000 and an organic polyisocyanate containing isocyanurate rings and having an average of more than two isocyanate groups per molecule.

2. A metallised film according to claim 1 in which the isocyanate-ended polyurethane in the resin coating is derived from an organic polyisocyanate and a polyhydroxy compound having a molecular weight greater than 400.

3. A metallised film according to claim 2 in which the organic polyisocyanate is selected from the group consisting of an aliphatic, a cycloaliphatic and an aromatic polyisocyanate.

4. A metallised film according to claim 3 in which the polyisocyanate is a diisocyanate.

5. A metallised film according to any one of the preceding claims in which the polyisocyanate containing isocyanurate rings is selected from the group consisting of an aliphatic, a cycloaliphatic and an aromatic polyisocyanate.

6. A metallised film according to any one of the preceding claims wherein the

relative proportions by weight of isocyanate-ended polyurethane and organic polyisocyanate containing isocyanurate rings are within the range 12:1 to 1:12.

- 5 7. A metallised film according to any one of the preceding claims in which the coating resin contains a waterproofing agent or a processing aid.
8. A metallised film according to any one of the preceding claims in which the film is of polypropylene or polyethylene terephthalate.
9. A metallised film according to any one of the preceding claims in which the film is a uni- or bi-axially oriented film.
10. A metallised film according to any one of the preceding claims metallised with a metal selected from the group consisting of zinc, aluminium, copper, chromium, nickel, silver and gold.
11. A process for producing a metallised organic thermoplastic polymeric film which comprises coating at least one surface of a film with a resin which contains an isocyanate-ended polyurethane of average molecular weight greater than 1000 and an organic polyisocyanate containing isocyanurate rings and having an average of more than two isocyanate groups per molecule, drying the coating on the film, and depositing a layer of metal on the

coated surface of the film.

12. A process according to claim 11 in which the resin is applied to the film surface as a dispersion or solution in a dispersant or solvent which does not react with isocyanates.

13. A process according to either of claims 11 and 12 in which the resin coating on the film surface is dried at a temperature of from 60 to 120°C, preferably from 60 to 90°C.

14. A process according to any one of claims 11 to 13 in which the layer of metal is deposited on the resin-coated surface of the film by a vacuum evaporation technique.

15. A process according to any one of claims 11 to 14 in which the film is treated to improve the bonding properties of the film before the resin coating is applied.

16. A process according to claim 11 for producing a metallised film substantially as herein described with particular reference to the Examples.

17. A metallised film whenever prepared by a process according to any one of claims 11 to 16.

18. A metallised film according to claim 1 substantially as hereinbefore described.

J. L. RHIND
Agent for the Applicants